Arabian Journal of Chemistry (2014) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Synthesis, dyeing performance on polyester fiber and antimicrobial studies of some novel pyrazolotriazine and pyrazolyl pyrazolone azo dyes

Hala F. Rizk, Seham A. Ibrahim *, Mohammed A. El-Borai

Tanta University, Faculty of Science, Chemistry Department, Tanta, Egypt

Received 28 April 2013; accepted 16 January 2014

KEYWORDS

Pyrazolotriazine;
Pyrazolyl pyrazolone;
Disperse dyes;
Dyeing parameters;
Fastness properties;
Antimicrobial activities

Abstract 5-Amino-4-heterylazo-3-phenyl-1*H*-pyrazoles (**2a**–**d**) were diazotized and coupled with malononitrile to give pyrazoloazo malononitrile which by heating in glacial acetic acid gave novel pyrazolo[5,1-*c*][1,2,4]triazine dyes (**3a**–**d**). Also, some diazopyrazolyl pyrazolone dyes (**4a**–**h**) were synthesized by diazotization of **2a**–**d** and coupled with some pyrazolone derivatives. The structure of the synthesized dyes was determined by elemental analysis and spectral data. All the synthesized compounds were applied as disperse dyes and their dyeing performance on polyester fabric was studied. The fastness and colorimetric properties were measured. The results revealed that the monoazo dyes have good fastness and good to moderate affinity to polyester fabric than diazo dyes. In addition, the synthesized dyes were screened for their antimicrobial activities against *Staphylococcus aureus*, *Pseudomonas aeruginosa* (Gram positive), *Bacillus subtitles*, *Escherichia coli* (Gram negative) and *Candida albicans*, *Aspergillus niger* (Fungi). The results revealed that most of the prepared dyes have high antibacterial activity.

1. Introduction

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile applications in various fields such as dyeing of textile fibers, coloring of different materials, biological medical studies and advanced applications in organic synthesis (Bareini 2009; Karipcin et al., 2010). Disperse dyes are very popular and important class for dyeing polyester fibers due to their brilliancy, wide range of hue excellent fastness properties, in addition to the environmental and economic reasons (Metwally et al., 2012). 5-Aminopyrazoles are very important class of heterocycles due to their biological and pharmacological activities (Tsai and Wang, 2005; Yang et al., 2009). These compounds often exhibit anti-inflammatory, herbicidal, fungicidal, bactericidal, and antipyretic activities (Kumar et al., 2005; Yang et al., 2009; Jung et al., 2002; Gudmundsson et al., 2005; Sung et al., 2011; Gyorgy et al., 2008; Chimichi et al., 2006). The pyrazolotriazine compounds have received much attention owing to their antibacterial, antiviral and antihypertensive

* Corresponding author. Tel.: +20 1009195323.
E-mail address: sehamabdelatif@yahoo.com (S.A. Ibrahim).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

1878-5352 © 2014 Production and hosting by Elsevier B.V. on behalf of King Saud University.
http://dx.doi.org/10.1016/j.arabjc.2014.01.008

activities. Moreover, they are used as key starting material for the synthesis of commercial arylazopyrazole dyes which have found application in dyes, biological, pharmacological and complexmetric titration (Lister et al., 1970; Ahmed et al., 2012; Menegatti et al., 2006; Tsai and Wang, 2005; Y W Ho 2005; Kandil et al., 2001). As a part of our continuous interest on 5-amino pyrazole derivatives we report here the synthes of some novel azo and disazo dyes having pyrazole moiety and study their applications as disperse dyes to polyester fabrics (M A El-Borai et al. 2011; M A El-Borai et al. 2011; M A El-Borai et al. 2010).

2. Experimental

Commercially available polyester fabrics were used for dyeing. The chemicals used for synthesis were obtained from Sigma–Aldrich and used without further purification, and the solvents were of spectroscopic grade.

2.1. Chemistry

Melting points were recorded on a Gallenkamp melting point apparatus and are reported uncorrected. The infrared spectra were recorded on Perkin–Elmer FTIR 1430 spectrophotometer using KBr disk technique. The ^{1}H NMR spectra were recorded on a Bruker AC spectrometer (300 MHz) at 25 °C in DMSO-d_6 with TMS as an internal standard. Chemical shifts are reported in ppm and results are expressed as δ values. Mass spectra were measured on a Finnigan MAT 8222 EX mass spectrometer at 70 eV. Ultraviolet–visible (UV–vis) absorption spectra were recorded on an SHIMADZO UV-3101PC spectrophotometer using 1.0 cm matched silica cell. Microanalysis was performed on Perkin–Elmer 2400 Elemental Analyzer at Microanalytical center at Cairo University. Reaction progress was monitored by thin layer chromatography (TLC) using benzene/acetone (2/1 by volume) as eluent. 3-Phenyl-1*H*-pyrazol-5-amine **1**, 3-methyl-1*H*-pyrazole-5-one and 3-methyl-1-phenyl-pyrazole-5-one were synthesized according to the previously reported methods (Quiroga et al., 2008; Davies, 1954; Koike et al., 1954).

2.1.1. Dyeing

2.1.1.1. Dyeing procedure. All applications and fastness properties of dye stuffs have been performed at Misr Spinning and Weaving Company, Central Q.C. Laboratories, Mehalla El-Kubra, Egypt. The prepared azo dyes were applied to polyester fiber. The dyeing procedures were carried out according to (M A El-Borai et al. 2009; M A El-Borai et al. 2007).

2.1.1.2. Fastness determination. Color fastness to light, washing, perspiration, and rubbing of the prepared dyes on polyester fabrics were studied using standard methods for the assessment of color fastness of textile (the *grey* scale) (Anon 1990). The obtained results are recorded in (Table 3).

2.1.1.3. Color measurement. The colorimetric parameters of the dyed polyester fabrics were determined on a reflectance spectrophotometer (Gretag-Macbeth CE 7000a), equipped with a D65/10° source and barium sulfate as standard blank, and three repeated measurement average settings. The obtained results are depicted in (Table 4) (See. Table 5).

2.1.1.4. Antimicrobial screening. The microorganisms used in this study included *Staphylococcus aureus*, *Pseudomonas aeruginosa* (Gram positive), *Bacillus subtitles*, *Escherichia coli* (Gram negative) and *Candida albicans, Aspergillus niger* (Fungi). The strains under study were obtained from Al Azhar University, Fermentation Biotechnology, and applied Microbiology (Farm-BAM). Bacteria were cultured on nutrient agar and the fungus was cultured on Sabouraud agar slopes. Antimicrobial activities of the synthesized compounds were tested in vitro on nutrient agar at 30 °C after 24 h by the cut-plug method according to Pridham et al. (1965).

2.2. Synthesis

2.2.1. General procedure for the synthesis of 3-phenyl- 5-amino-4-hetarylazopyrazoles (*2a–d*)

A solution of sodium nitrite (0.651 g, 9.4 mmol) was gradually added to a cold solution (0 °C) of appropriate heterocyclic amines (9.4 mmol) in conc. HCl (8.5%, 3 ml). The diazonium salt obtained was added with continuous stirring to a cold solution (0 °C) of 3-phenyl-1*H*-pyrazol-5-amine **1** (1.13 g, 6.5 mmol) in ethanol (35 ml) containing sodium acetate (2.5 g). The reaction mixture was stirred at 0 °C for 2 h and the colored solid formed was filtered, washed with water and crystallized from ethanol to give compounds **2a–d**.

3-Phenyl-4-(pyrazin-2-yldiazenyl)-1H-pyrazol-5-amine (**2a**) yield 70%, m.p. 240–242 °C.FTIR (KBr): ν_{max}: 1597(N=N), 3178(NH_2) cm^{-1} ^{1}H NMR[300 MHz,DMSO-d_6]: δ = 8.20(s, 2H, NH_2), 7.10–8.60(m,8H, Ar-H) ppm.Anal. for $C_{13}H_{11}N_7$()-calcd: C, 58.86; H, 4.18; N, 36.96. Found C, 58.26; H, 4.09; N, 36.78%; MS: *m*/*z* 265.

4-((1H-Imidazol-2-yl) diazenyl)-3-phenyl-1H-pyrazol-5-amine (**2b**) yield 69%, m.p. 260–263 °C). FTIR (KBr): ν_{max}: 1578(N=N), 3100(NH_2) cm^{-1} ^{1}H NMR[DMSO-d_6]: δ 9.10(s, 2H, NH_2), 11.90(s, 1H, NH of Imidazole ring), 7.20–8.30(m,7H, Ar-H)ppm.Anal. for $C_{12}H_{11}N_7$()calcd: C, 56.91; H, 4.38; N, 38.71.Found C, 56.74; H, 4.21 N, 38.55%; MS: *m*/*z* 254.

3-Phenyl-4-(thiazol-2-yldiazenyl)-1H-pyrazol-5-amine (**2c**) yield 80%, m.p. 250–251 °C).FTIR (KBr): ν_{max}: 1571(N=N), 3294(NH_2) cm^{-1} ^{1}H NMR[300 MHz,DMSO-d_6]: δ 9.30(s, 2H, NH_2), 6.20–8.20(m,7H, Ar-H)ppm. Anal. for $C_{12}H_{10}N_6S$ calcd: C, 53.32; H, 3.73; N, 31.09; S, 11.86. Found C, 53.52; H, 3.33; N, 31.04; S, 11.45%; MS: *m*/*z* 272.

4-((5-Amino-3-phenyl-1H-pyrazol-4-yl)diazenyl)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (**2d**) yield 76%, m.p. 230–232 °C.FTIR (KBr): ν_{max}: 1554(N=N), 3159(NH_2) cm^{-1} ^{1}H NMR[DMSO-d_6]: δ 2.10(s, 3H, CH_3), 2.40(s, 3H, N-CH_3), 8.30(s, 1H, NH_2), 7.10–8.20 (m,10H, Ar-H). Anal. for $C_{20}H_{21}N_7O$ calcd: C, 64.33; H, 5.13; N, 26.26. Found C, 64.11; H, 5.17; N, 26.26%; MS: *m*/*z* 374.

2.2.2. General procedure for the synthesis of 7-amino-6-cyano-2-phenyl-3- substituted azopyrazolo [5, 1-c] [1, 2, 4] triazine (*3a–d*)

Nitrosylsulfuric acid was prepared by dissolving sodium nitrite (1 g) in sulfuric acid (7 ml) at 0 °C. 5-Amino-3-phenyl-4-*substituted* azo-1H-pyrazole (**2a–d**) (2 mmol) was dissolved in hot

glacial acetic acid (2.5 ml) and rapidly cooled in ice/salt bath to 0–5 °C. The solution was added in portions over 30 min to nitrosylsulfuric acid at 0–5 °C and the mixture stirred for a further 1 h at this temperature. The resulting diazonium solution was added in portions over 30 min to a vigorously stirred solution of malononitrile (1.32 g, 2 mmol) in pyridine (10 ml), maintaining the pH at 7–8 by addition of solid sodium acetate at 0–5 °C. The mixture was stirred for 2 h at 0–5 °C. The resulting solid was filtered, washed with cold water (3 × 50 mL). A solution of the precipitated solid in glacial acetic acid (30 ml) was refluxed for 4 h. The solvent was evaporated in vacuo and the remaining product was collected by filtration, dried in air and crystallized from DMF-H_2O (3:1) to give compounds **3a–d**.

*4-Amino-7-phenyl-8-(pyrazin-2-yldiazenyl)pyrazolo[5,1-c][1,2,4]triazine-3-carbonitrile(**3a**)* yield 70%, m.p. 185–187 °C. FTIR (KBr): ν_{max}: 1554(N═N), 3159 (NH_2) cm^{-1} ^1H NMR[DMSO-d_6]: δ 8.40(s, 2H, NH_2), 7.10–8.20(m,8H, Ar-H)ppm.Anal. for $C_{16}H_{10}N_{10}$ calcd: C, 54.54; H, 3.05; N, 42.41. Found C, 54.44; H, 3.14; N, 42.55%;MS: m/z 342.

*8-((1H-Imidazol-2-yl)diazenyl)-4-amino-7-phenylpyrazolo[5,1-c][1,2,4]triazine-3-carbonitrile(**3b**)* yield 69%, m.p. 175–176 °C.FTIR (KBr): ν_{max}: 1554(N═N),3159(NH_2)cm^{-1} ^1H NMR[DMSO-d_6]ppm: δ 9.47(s, 2H, NH_2), 12.50(s, 1H, NH of Imidazole ring), 7.20–8.30(m,7H, Ar-H).Anal. for $C_{15}H_{10}N_{10}$ calcd: C, 54.54; H, 3.05; N, 42.41. Found C, 54.44; H, 3.14; N, 42.55%; MS: *m/z* 328.

4-Amino-7-phenyl-8-(thiazol-2-yldiazenyl)pyrazolo[5,1-c][1,2,4]triazine-3-carbonitrile (**3c**) yield 80%, m.p. 220–221 °C.FTIR (KBr): ν_{max}: 1554(N═N), 3159(NH_2) cm^{-1} ^1H NMR[DMSO-d_6]: δ 9.47(s, 2H, NH_2), 6.60–8.30(m,7H, Ar-H)ppm.Anal. for $C_{15}H_9N_9S$ calcd: C, 51.87; H, 2.61; N, 36.29; S, 9.23Found C, 51.23; H, 2.71; N, 36.55; S, 9.43%; MS: *m/z* 347.

*4-((4-Amino-3-methyl-7-phenylpyrazolo[5,1-c][1,2,4]triazin-8-yl)diazenyl)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one(**3d**)* yield 76%, m.p. 240–242 °C.FTIR (KBr): ν_{max}: 1554(N═N), 3159(NH_2) cm^{-1} ^1H NMR[DMSO-d_6]: δ 2.07(s, 3H, CH_3), 2.60(s, 3H, N–CH_3), 8.40(s, 1H, NH_2), 7.40–8.00 (m,10H, Ar-H)ppm.Anal. for $C_{23}H_{18}N_{10}O$ calcd:

Table 1 Absorption spectra of compounds **2a–d**, **3a–d** and **4a–h**.

Cpd. no.	Het	R	Absorption λ_{max} (nm)	Logε
2a	Pyrazine ring	–	400	4
2b	Imidazole ring	–	474	3.99
2c	Thiazole ring	–	404	3.97
2d	Antipyrine ring	–	400	4.33
3a	Pyrazine ring	–	463	4.05
3b	Imidazole ring	–	511	3.99
3c	Thiazole ring	–	514	4.29
3d	Antipyrine ring	–	487	4.23
4a	Pyrazine ring	H	375	4.03
4b	Imidazole ring	H	406	4.02
4c	Thiazole ring	H	384	2.98
4d	Antipyrine ring	H	406	4.38
4e	Pyrazine ring	Ph	367	4.14
4f	Imidazole ring	Ph	405	3.03
4g	Thiazole ring	Ph	382	4.29
4h	Antipyrine ring	Ph	403	4.33

Table 2 Fastness properties of dyes 2a-d, 3a-d, and 4a-h on polyester fabric[a].

Dye. no	Colour	Washing		Perspiration		Rubbing		Sublimation		light
		PES	Cotton	PES	Cotton	Dry	Wet	PES	Cotton	
2a	Dark brown	3-4	3	3-4	3-4	3	3	3-4	3-4	4
2b	Light brown	3-4	3-4	3-4	3-4	3	3	3	3	4
2c	Orange	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4
2d	Brown	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4
3a	Brown	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	5-6
3b	Reddish brown	4	4	3-4	3-4	4-5	4	4	4	6
3c	Brown	3-4	3-4	3-4	3-4	4-5	4	4	4	6
3d	Reddish brown	3-4	3-4	3	3	4-5	4	4	4	6
4a	Brown	3-4	3-4	3	3	4-5	4	4	4	6
4b	Yellow	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4	6
4c	Light brown	3-4	3-4	3	3	4	3-4	3-4	4	6
4d	Light brown	3-4	3-4	3	3	3-4	3-4	4	3-4	6
4e	Yellow	3-4	3-4	3-4	3-4	3-4	3-4	4	4	6
4f	Brown	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4	6
4g	Light brown	3-4	3-4	3-4	3-4	3-4	3-4	4	4	5
4h	Light - brown	3-4	3-4	3-4	3-4	4	3-4	4	3-4	5

[a] Rate for light fastness: 4–8 (acceptable), 1–3 (not acceptable); rate for different fastness: 3–4 (acceptable), 1–2 (not acceptable).

Please cite this article in press as: Rizk, H.F. et al., Synthesis, dyeing performance on polyester fiber and antimicrobial studies of some novel pyrazolotriazine and pyrazolyl pyrazolone azo dyes. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.01.008

Table 3 Color of the dyes **2a–d**, **3a–d** and **4a–h** on polyester fabrics.

Dye	L*	a*	b*	c*	% R	K/S
2a	47.25	−.5	−0.34	1.22	13.03	2.9
2b	68.16	6.76	26.96	27	14.96	2.4
2c	54.8	31.4	45.03	52.5	3.61	14.83
2d	57.5	7.51	38.9	37.8	4.36	10.48
3a	39.58	18.6	22.55	29.7	3.31	14.12
3b	39.93	7.4	19.15	18.4	3.7	12.53
3c	54.62	31.2	45	55	3.1	14.99
3d	44.24	10.9	27	30	3.09	15.51
4a	84.63	−1.2	18.62	18.2	38.9	0.47
4b	78.1	−8.9	37.89	38.5	15.15	2.37
4c	68.66	6.5	26.6	32.9	15.22	2.36
4d	76.4	11.9	17.74	45	29.8	0.82
4e	80.77	−0.6	34.38	40	21	1.48
4f	57.4	7.47	39.19	14.9	4.3	10.64
4g	69	6.39	26.7	27.5	14	12.5
4h	69.1	24.5	23.89	34	18.57	1.78

C, 61.93; H, 4.55; N, 30.09. Found C, 61.77; H, 4.74; N, 30.11%; MS: *m*/*z* 450.

2.2.3. General procedure for the synthesis of 5-(3/-phenyl-4/-hetarylazo-1/H-pyrazol-5/-ylazo-3-methyl-5-hydroxy-pyrazole (4a–h)

5-Amino-3-phenyl-4-(substituted hetarylazo)-1H-pyrazole (**2a–d**) (2 mmol) was dissolved in hot glacial acetic acid (2.5 ml) and rapidly cooled in an ice-salt bath at 0–5 °C. The solution was then added in portions over 30 min to nitrosyl sulfuric acid at 0–5 °C and the mixture was stirred for a further 1 h at this temperature. The resulting diazonium solution was added in portions over 30 min to a vigorously stirred solution of 3-methyl-1*H*-pyrazole-5-one (0.196 g, 2 mmol) and/or 3-methyl-1-phenyl-pyrazole-5-one (0.348 g, 2 mmol) in potassium hydroxide (0.11 g, 2 mmol) and water (2 ml) at 0–5 °C. The pH of the coupling mixture was maintained at 5–6 by adding solid sodium acetate. The mixture was stirred for 1 h at 0–5 °C; the resulting solid was filtered, washed with cold water (3 × 30 mL) and dried in air, crystallized from DMF/H_2O (1:1) mixture to give compounds **4a–h**.

3-Phenyl-4-(pyrazin-2-ylazo)-5-(3-methyl-1-H-5-pyrazolon-4-ylazo)-1H-pyrazole(**4a**) yield 60%, m.p. 130–131 °C.FTIR (KBr): ν_{max}: 1518(N═N),1670(C═O), 3327(NH) cm^{-1} ^1H NMR[DMSO-d_6]: δ 2.40(s,3H,CH_3),7.17(s,1H,CH), 10.54 (s,1H,NH of pyrazole ring), 11.70(s,1H, NH of pyrazolone ring),12.50(s,1H,OH or NH), 7.48–8.45(m,7H, Ar-H)ppm. Anal. for $C_{20}H_{17}N_5O_2$ calcd: C, 54.54; H, 3.77; N, 37.42. Found C, 54.56; H, 3.97; N, 37.48%; MS: *m*/*z* 374.

3-Phenyl-4-(1H-imidazol-2-ylazo)-5-(3-methyl-1H-5-pyrazolon-4-ylazo)-1H-pyrazole (**4b**) yield 45%, m.p. 200–202 °C. FTIR (KBr): ν_{max}: 1633(N═N) and 1711(C═O), 3413 (NH)cm^{-1}. ^1H NMR[DMSO-d_6]: δ 2.07(s,3H,CH_3), 6.60(s,1H,CH), 11.05 (s,1H, NH of imidazole ring), 11.20 (s,1H, NH of pyrazole ring), 12.10(s,1H, NH of pyrazolone ring), 12.50(s,1H,OH or NH), 6.90–8.80(m,7H, Ar-H)ppm Anal. for $C_{16}H_{14}N_{10}O$ calcd: C, 53.03; H, 3.89; N, 38.66. Found C, 53.11; H, 3.79; N, 38.86%; MS: *m*/*z* 362.

3-Phenyl-4-(1,3-thiazol-2-ylazo)-5-(3-methyl-1H-5-pyrazolon-4-ylazo)-1H-pyrazole (**4c**) yield 45%, m.p. 200–202 °C.FTIR (KBr): ν_{max}: 1573(N═N),1691(C═O), 3396(NH)cm^{-1}.^1H NMR[DMSO-d_6]: δ 2.30(s,3H,CH_3),6.90(-s,1H,CH),10.70(s,1H,NH of pyrazole ring),11.70(s,1H, NH of pyrazolone ring),12.50(s,1H,OH or NH),7.40–8.20(m,7H, Ar-H)ppm. Anal. for $C_{16}H_{13}N_9OS$ calcd: C, 50.65; H, 3.45; N, 33.23; S, 8.45. Found C, 50.78; H, 3.45; N, 33.77; S, 8.35%; MS: *m*/*z* 380.

3-Phenyl-4-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-ylazo)-5-(3-methyl-1H-5-pyrazolon-4-ylazo)-1H-pyrazole(**4d**) yield: 50%, m.p. 170–172 °C. FTIR (KBr): ν_{max}: 1638 (N═N),

Table 4 Diameters of inhibition zones (mm) of newly synthesized compounds against different test bacteria and fungi on nutrient agar at 30^0C after 24 h[b].

Compound	*Bacillus subtilis*	*E.coli*	*Staphylococcus aureus*	*Pseudomona saeruginosa*	*Candida albicans*	*A.nigar*
2a	−ve	−ve	13	12	15	−ve
2b	−ve	−ve	−ve	−ve	14	−ve
2c	24	27	26	25	26.5	
2d	−ve	−ve	−ve	−ve	−ve	−ve
3a	42	20	21	21.5	21	15
3b	20.5	20	21	20.5	22	18
3c	16	21.5	16	16.5	17	−ve
3d	17	19	15	18	15.5	−ve
4a	18	21	20	17	20	−ve
4b	16	16	18	16.5	17	−ve
4c	15.5	17	19	18	18	−ve
4d	−ve	−ve	−ve	−ve	−ve	−ve
4e	−ve	−ve	−ve	−ve	−ve	−ve
4f	17.5	24	–	16	15.5	−ve
4g	20	24	21	22	23.5	−ve
4h	19	22	19	21	20	−ve
St	31.5	30	32	37.5	25	23

St = Standard Miphinicol was used at conc.1 mg/ml for gram positive bacteria, while Keflex was used as standard for gram negative bacteria at conc 1 mg/ml. Flucoral was used as standard for fungi at conc. 1 mg/ml. Amikacin was tested as standard at conc 1 mg/ml for *candida albicans*.

[b] The concentration used is 10 mg/mL. Control disks were performed in DMSO (dimethylsulfoxide) and no zones of inhibitions were observed. –ve = resistant.

Please cite this article in press as: Rizk, H.F. et al., Synthesis, dyeing performance on polyester fiber and antimicrobial studies of some novel pyrazolotriazine and pyrazolyl pyrazolone azo dyes. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.01.008

Table 5 Minimal inhibitory concentration (MIC) of the provided samples against test microorganisms (MIC) μg/ml.

Compound	*Bacillus subtilis*	*E.coli*	*Staphylococcus aureus*	*Pseudomonasaeruginosa*	*Candida albicans*	*A.nigar*
3a	62.5	125	125	62.5	62.5	1000
3b	125	62.5	31.25	62.5	62.5	1000
St	31.25	62.5	31.25	62.5	31.25	1000

All the dilutions of both samples and standards were performed by double fold dilution.

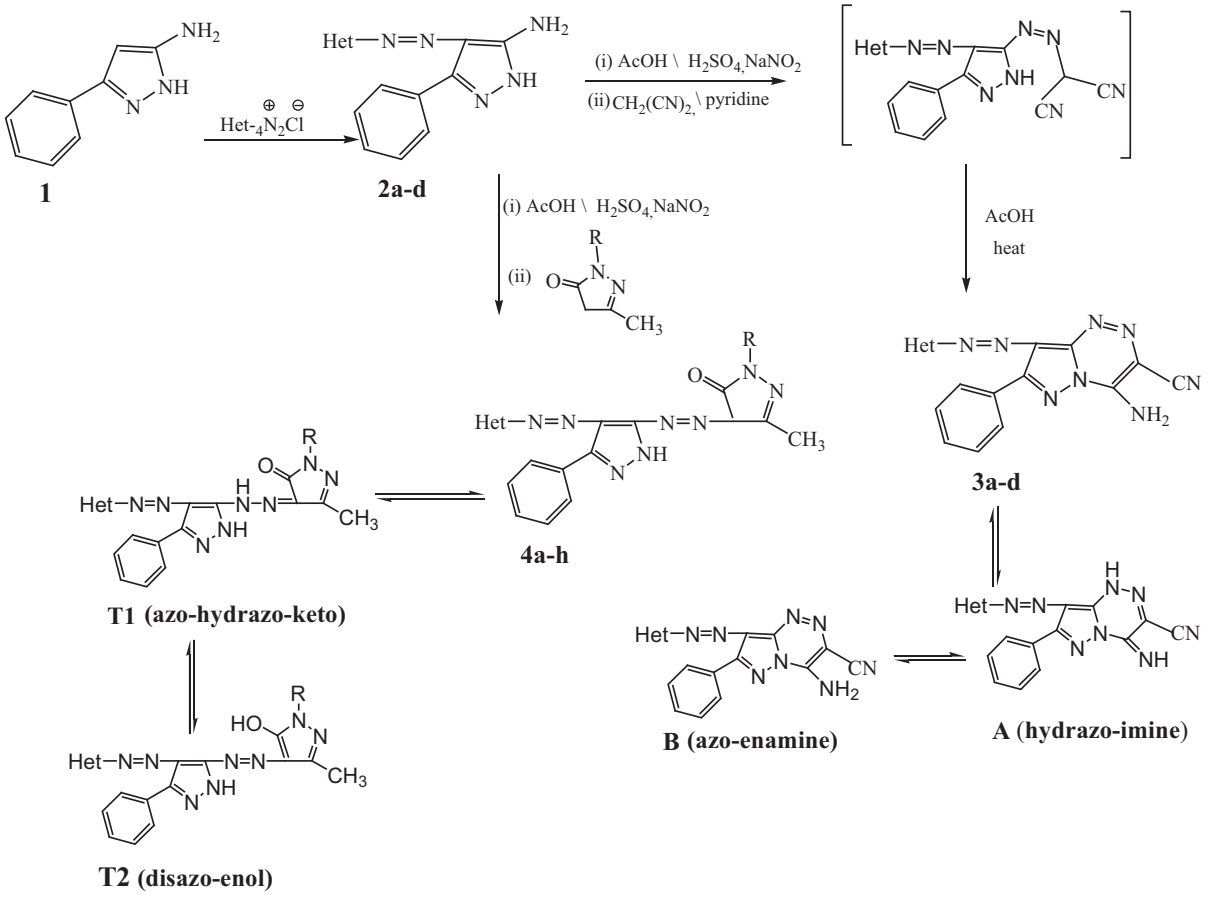
1657 (C═O), 3425(NH) cm^{-1}. ^1H NMR[DMSO-d_6]: δ 2.07(s,3H,CH_3),2.16(s,3H,CH_3),2.60(s,3H,N-CH_3), 6.90(s,1H, CH),10.50 (s,1H,NH of pyrazole ring),11.70(s,1H, NH of pyrazolone ring),12.80(s,1H,OH or NH),7.39–8.25 (m,10H, Ar-H)ppm. Anal. for $C_{24}H_{22}N_{10}O_2$ calcd: C, 59.74; H, 4.60; N, 29.03. Found C, 59.88; H, 4.59; N, 29.03%; MS: *m*/*z* 483.

3-Phenyl-4-(pyrazin-2-ylazo)-5-(3-methyl-1-phenyl-5-pyrazolon-4-ylazo)-1H-pyrazole (**4e**) yield 54%, m.p. 205–207 °C. FTIR (KBr): ν_{max}: 1633(N═N),1700(C═O),3425(NH)cm^{-1}. ^{1}HNMR[DMSO-d_6]: δ 2.37(s,3H,CH_3),6.90(s,1H,CH),13.55 (s,1H,NH of pyrazole ring), 14.54 (s,1H,OH or NH), 7.06–8.6 (m,12H, Ar-H) ppm. Anal.calcd for $C_{23}H_{18}N_{10}O$: C, 61.33; H, 4.03; N, 31.09.Found C, 61.33; H, 4.10; N, 31.27%; MS: *m*/*z* 450.

3-Phenyl-4-(1H-imidazol-2-ylazo)-5-(3-methyl-1phenyl-5-pyrazolon-4-ylazo)-1H-pyrazole (**4f**) yield 54%; m.p. 205–207 ° C.FTIR (KBr): ν_{max}: 1637(N═N),1699(C═O), 3434(NH) cm^{-1} ^1H NMR[DMSO-d_6]: δ 2.37(s,3H,CH_3),7.2(s,1H,CH), 13.5(s,1H,NH of imidazole ring),14(s,1H, NH of pyrazole ring),14.5(s,1H,OH or NH), 7.7–8.2 (m,12H, Ar-H)ppm. Anal. for $C_{22}H_{18}N_{10}O$ calcd: C, 60.27; H, 4.14; N, 31.95. Found C, 59.99; H, 4.19; N, 31.78%; MS: *m*/*z* 438.

3-Phenyl-4-(1,3-thiazol-2-ylazo)-5-(3-methyl-1phenyl-5-pyrazolon-4-ylazo)-1H-pyrazole (**4g**) yield 59%, m.p. 225–227 °C.FTIR (KBr): ν_{max}: 1539(N═N),1627(C═O),3326 (NH)cm^{-11}H NMR[DMSO-d_6]: δ 2.30(s,3H,CH_3), 6.60(s,1H, CH),12.80(s,1H,NH of pyrazole ring), 13.50(s,1H,OH or NH), 6.90–8.60(m,12H, Ar-H)ppm. Anal. for $C_{22}H_{17}N_9OS$ calcd: C, 58.01; H, 3.76; N, 27.68; S, 7.04.Found C, 58.11; H, 3.76; N, 27.96; S, 7.11%; MS: *m*/*z* 455.

3-Phenyl-4-(2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-ylazo)-5-(3-methyl-1phenyl-5-pyrazolon-4-ylazo)-1H-pyrazole (**4h**) yield 60%, m.p. 260–261 °C.FTIR (KBr): ν_{max}: 1583(N═N),1649(C═O), 3421(NH)cm^{-1} ^1H NMR[DMSO-d_6]: δ 2.30(s,3H,CH_3),2.37(s,3H,CH_3),2.60(s,3H,N-CH_3), 7.00 (s,1H,CH),13.59 (s,1H,NH of pyrazole ring), 13.70(s,1H,OH



Scheme 1

or NH), 7.20–8.60 (m,15H, Ar-H)ppm. Anal. for $C_{30}H_{26}N_{10}O_2$ calcd: C, 58.01; H, 3.76; N, 27.68.

Found C, 58.17 H, 3.55; N, 27.97%; MS: *m*/*z* 559.

3. Results and discussion

We report here the synthesis of a series of monoazo dyes based on pyrazolo[5,1-*c*][1,2,4] triazine (**3a–d**) by coupling of 5-amino-3-phenyl-1*H*-pyrazole **1** with a variety of heterocyclic diazonium salts to give the corresponding 3-phenyl-5-amino-4-heteroazo-1*H*-pyrazoles (**2a–d**) in good yield (Scheme 1). The IR spectra of compound (**2a–d**) showed the characteristic absorption bands at γ1554–1597 cm^{-1} for the azo group and at γ 3378–3427 cm^{-1} for the amino group at position **5**. The diazotization of **2a–d** was followed by coupling with malononitrile in pyridine at pH 7–8, the formed solid was filtered quickly and refluxed in glacial acetic acid to give compounds **3a–d** (Scheme 1). Azo dyes **3a–d** can exist in two possible tautomeric forms, namely the azo-enamine form **A** and the hydrazo-imine form **B** as shown in (Scheme 1). The IR spectra of compounds **3a–d** showed the characteristic absorption band group at γ 2207–2216 cm^{-1} for the Cyano group, at γ 1583–1587 cm^{-1} for the azo group and a broad band at 3159 cm^{-1} for the amino group. Furthermore, the ^1H NMR spectra of compounds **3a–d** showed the presence a singlet attributed to amino protons at δ 8.40–9.47 ppm and multiplet at δ 7.05–8.30 ppm corresponding to heteroaromatic moieties, which confirm the azo-enamine form **B** for these compounds. The heterocyclic diazo pyrazolone dyes (**4a–h**) were prepared by coupling 3-phenyl-1*H*-pyrazole-5-one and 1, 3-diphenyl-pyrazole-5-one with diazotized 5-amino-3-phenyl-4-hetarylazo-1*H*-pyrazoles (Scheme 1). The ^1H NMR spectra of dyes **4a–h** showed a singlet at δ 2.07–2.40 ppm (CH_3 of pyrazolone ring), a broad peak at δ 12.5–14.5 ppm for –OH or –NH protons (enol or hydrazo forms of pyrazolone ring), a broad peak at δ 11.7–14.00 ppm for –NH protons (1-*H* of pyrazolone ring) and a broad peak at δ 10.54–11.20 ppm for –NH protons (1-*H* of pyrazole ring). The obtained results revealed that the prepared dyes are in favor of the predominantly single tautomeric form (T1 or T2 as shown in scheme 1), the mass spectral data confirm the structure of all the synthesized compounds (see. Experimental).

4. UV–vis spectroscopic analysis of dyes 2a–d, 3a–d, and 4a–h

It is well known that heterocyclic based azo disperse dyes tend to gave a pronounced bathochromic shift compared to the corresponding benzenoid compounds (Hallas and Choi, 1999; Joerg et al., 1988), with larger solvatochromic effects due to the increasing polarity of the dye system, especially in the excited state.

The electronic spectra showed λmax at 400–474 nm for dyes **2a–d**, and λ_{max} 463–514 nm for the prepared dyes **2a–d**, **and 3a–d** respectively (Table 1). These bands were due to electronic transitions involving the whole conjugate system (both of the phenyl rings, heterocyclic moieties and the azo group which assigned to a transition of π–π* type).The introduction of the cyano group as an electron withdrawing subsistent onto compounds **3a–d** produces a bathochromic shift of the absorption band. This is attributed to more extensive electron delocalization and small steric requirements of the rod-like cyano group (Hiremith et al., 2002), the obtained results are depicted in (Table 1).

The electronic spectra of the compounds **4a–h** showed a band at λ_{max} 375–406 nm due to the π–π*excitation of the electrons of the azo groups. It is worthy to note that the absorbance bands for biazopyrazolyl pyrazolone dyes **4a–h** located in the region λ_{max} 375–406 nm are due to deformation of the functional groups.

5. The dyeing properties of the prepared dyes on polyester fabrics

The results obtained are depicted in (Table 2), having the following observations:

(a) The dyed fabrics **3b**, **3c**, **3d**, **4a** exhibit excellent (4–5) washing, perspiration, sublimation and rubbing fastness properties, while dyes **2a–d**, **3a**, **4b–h** exhibit good (3–4) washing, perspiration, sublimation and rubbing fastness properties.
(b) The light fastness of dyed fabrics exhibit moderate to very good (5–6) fastness properties for all the synthesized dyes.

6. Color assessment

The assessment of color-dyed fabrics was made in terms of tristimulus colorimetry. The following CIELAB coordinates are measured, lightness (L*), chroma (c*), hue angle from 0 °C to 360 °C (h), (a*) value represents the degree of redness (positive) and greenness (negative) and (b*) represents the degree of yellowness (positive) and blueness (negative). The measured *K*/*S* values given by the reflectance spectrometer are directly correlated with the dye concentration on the dye substrate according to the KubelkaeMunk equation: $K/S = (1-R)^2/2R$. Where *K* = absorbance coefficient, *S* = scattering coefficient, *R* = reflectance ratio. The color coordinates indicate that the dyes have good affinity to polyester fabrics with the following conclusions (Table 3):

(a) The color hues of the dyes under investigation on polyester fabric are shifted to the yellowish direction on the yellow-blue axis according to the positive values of b*, while the color hues of the **2a** (−0.49) are shifted to the bluish direction on the yellow-blue axis as according to the negative values of b* for these dyes.
(b) The color hue of the dye **2a**, **4a**, **4b** on polyester fabric is shifted to the greenish direction on the red green axis as indicated from the negative value of a* (−1.11, −1.62, −8.97 respectively), while the color hues of the other synthesized dyes on polyester fabrics are shifted to the reddish direction on the red green axis as according to the positive values of a* for the prepared dyes.
(c) The **2b**, **4a–e**, **4e**, **4h**, **4g**, dyes are more light than the corresponding dyes **2a**, **2c**, **2d**, **4a–d**, **5f** according to the color lightness values (L*).
(d) The **2c**, **d**, **3c**, **4b**, **e**, **f**, **h** dyes are brighter than the corresponding dyes **2a**, **b**, **3a**, **b**, **d**, **4a**, **c**, **d**, **g** according to the color brightness value (C*).

Please cite this article in press as: Rizk, H.F. et al., Synthesis, dyeing performance on polyester fiber and antimicrobial studies of some novel pyrazolotriazine and pyrazolyl pyrazolone azo dyes. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.01.008

(e) K/S values in the dyes under investigation **2a–d**, **3a–d** and **4a–h** vary from 0.47 to 15.51. Dyes **2a**, **c** and **3a–d** are characterized by higher K/S values compared with the other dyes, indicating that the color strength on polyester fabrics increases at high temperature and gave generally deep and bright intense hues, ranging from yellow to reddish brown, while dyes **4a–h** showed less affinity due to large and asymmetric structure of the dyes which prevent the substantivity of dyes on fiber.

7. Antimicrobial activity

The antibacterial and anti-fungal activities of the dyes were determined against four bacteria *S. aureus*, *P. aeruginosa* (Gram positive), *B. subtitles*, *E. coli* (Gram negative) and *C. albicans*, *A. niger* (fungi). Results of the antimicrobial tests are presented in (Table 4). All the tested compounds except **2a**, **2b**, **2d**, **4d**, **4e** exhibited strong activity against all strains of tested organisms. For antifungal activity among the compounds tested only compounds **3a**, **3b** were active against the *A. niger fungi*. *On the other hand* **2d**, **4d**, **4e** exhibited inactivity against *C. albicans*.

8. Conclusions

In this work, a series of new monoazo dyes based on pyrazolo [5, 1-c] [1, 2, 4] triazine ring **3a–d**, the heterocyclic series of disazo pyrazolone dyes **4a–h** have been synthesized. The characterization and the absorption ability of novel disperse dyes **3a–d**, **4a–h** were studied. All the synthesized compounds were applied to polyester fabrics as disperse dyes. The fastness and colorimetric properties were measured. The results revealed that the monoazo dyes have good fastness and good to moderate affinity to polyester fiber than diazo dyes and also significant antimicrobial activity, the results revealed that all compounds except **2a**, **2b**, **2d**, **4d**, **4e** compounds exhibited antibacterial activity of high order against all strains of the bacteria used. For antifungal activity the tested compounds except **2d**, **4d**, **4e** exhibited activity against *C. albicans,* while only compounds **3a**, **3b** were active against *A. niger fungi*.

References

Ahmed, Z.S., Mahmoud, S.A., Hesham, S.N., 2012. J .Mol. Struc 1010, 146.
Anon; Standard Methods Forte Determination of the Color Fastness of Textiles and Leather, 5th edn, Society of Dyes and Colorists publication, Bradford, England, (1990).
Bareini, Z., 2009. Pigm. Resin Technol. 5, 298.
Chimichi, S., Boccalini, M., Hassan, M.M.M., Viola, G., DallÁcqua, F., Curini, M., 2006. Tetrahedron 62, 90.
Gudmundsson, K.S., Johns, B.A., Wang, Z., Turner, E.M., Allen, S.H., Freeman, G.A., Lesleboyd, F., Sexton, C.D., Sellseth, D.W., Moniri, K.R., Greeh, K.L., 2005. Bioorg. Med. Chem. 13, 5346.
Gyorgy, S., Janos, F., Klara, G., 2008. J. Med. Chem. 51, 142.
Hiremith, S.P., Rudresh, K., Saundan, A.R.I., 2002. Indian J. Chem. 41B (2), 394.
Hallas, G., Choi, J.H., 1999. Dyes Pigm. 40 (2-3), 99.
Joerg, S., Reinhold, G., Otto, S., Joachim, S, H., Robert, S., Klaus, L., Ger Offen, 04 Feb 1988; DE 3, 625, 686 (Cl C07D 231/22) [C.A. 108167465(1988)].
Jung, J.C., Walkins, E.B., Avery, M.A., 2002. Tetrahedron 58, 3039.
Karipcin, F., Dede, B., Percin-Ozkorucuklu, S., 2010. Dyes Pigm. 84, 14.
Kandil, S.S., Abdel-Hay, F.I., Issa, R.M., 2001. J. Therm. Anal. Calorim. 68, 173.
Kumar, V., Aggarwal, R., Tyagi, P., Singh, S., 2005. Eur. J. Med. Chem. 40, 922.
Koike, Iida, Okawa, Kashioka., 1954. J. Chem. Soc. 57, 56.
Lister, J.H., Manners, D.S., Timmis, G.M., 1970. J. Chem. Soc. Chem. Commun. 9, 1313.
Menegatti, R., Silva, G.M.S., Zapata, G., Sudo, J.M., Raimundo, R.T., Sudo, E.J., 2006. Bioorg. Med. Chem. 14, 677.
Metwally, M.A., Abdel-Galil, E., Metwally, A., Amer, F.A., 2012. Dyes Pigm. 92, 902.
Pridham, T.G., Lindenfelser, L.A., Shotwell, O.L., Stodola, F., Benedict, R.G., Foley, C., Jacks, P.W., Zaumeyer, W.J., Perston, W.H., Mitchell, J.W., 1965. Phytopathology 46, 568.
Quiroga, J., Portilla, J., Abonia, R., Insuasty, B., Nogueras, M., Cobo, J., 2008. Tetrahedron Lett. 49, 6254.
Rizk, H.F., EI-Badawi, M.A., Ibrahim, S.A., El-Borai, M.A., 2011. Chin. J. Chem. 29, 1451.
Rizk, H.F., EI-Badawi, M.A., Ibrahim, S.A., El-Borai, M.A., 2010. J. Korean. Chem. Soc. 154, 737.
Rizk, H.F., EI-Badawi, M.A., Ibrahim, S.A., El-Borai, M.A., 2011. Arabian. J. Chem. 4, 25.
Rizk, H.F., El-Borai, M.A., El-Hefnawy, G.B., El-Sayed, H.F., 2009. Chin. J. Chem. 27, 1359.
Rizk, H.F., EI-Badawi, M.A., Ibrahim, S.A., El-Borai, M.A., 2007. Indian J. Org. Chem.(TSI). 4, 115.
Sung, H.H., Karen, M.W., Aaron, T.W., Bruce, D.H., 2011. J. Med. Chem. 54, 3037.
Tsai, P.C., Wang, I.J., 2005. Dyes Pigm. 64, 259.
Wiley, Hart, Davies, Smith. 1954.J. Am. Chem. Soc. 76, 4931.
Yang, B., Yuan, L., Chao-Jun, C., Jian-Ping, C., Meng-Shen, C., 2009. Dyes Pigm. 83, 144.
Y W Ho., 2005. Dyes Pigm. 64, 223.

Please cite this article in press as: Rizk, H.F. et al., Synthesis, dyeing performance on polyester fiber and antimicrobial studies of some novel pyrazolotriazine and pyrazolyl pyrazolone azo dyes. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.01.008